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(12) DESCRIPTION OF INVENTION
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(56) 1. US Patent No. 4096163, cl. C 07 C 1/04 (1978). 2. US Patent No. 4180516, cl. C 07 C 1/04 (1979). 3. US Patent No. 4086262, cl. C 07 C 1/04 (1978). 4. EPB Application No. 004469, cl. C 07 C 1/02 (1984).

(54) METHOD FOR PRODUCTION OF NAPHTHA CUT HYDROCARBONS

(57) The invention concerns organic chemistry, namely, petrochemistry, and in particular, a method for production of naphtha hydrocarbons by catalytic conversion of a mixture of CO_2 and H_2 and/or a mixture of CO_2 , CO , and H_2 . The content of aromatic hydrocarbons in naphtha cuts with a high degree of conversion of CO_2 , H_2 , and CO is increased because type ZSM-5 or ZSM-11 zeolite is used as the zeolite component of the catalyst and a composite of three or more metal oxides of the general formula

$a \text{ CuO } b \text{ ZnO } c \text{ Al}_2\text{O}_3 \text{ d } \text{Cr}_2\text{O}_3 \text{ and } \text{W}_2\text{O}_5$

is used as the metal oxide component, where a, b, c, d, and e are the mass fractions of metal oxides in the metal oxide component; $a = 0-56$, $b = 24-67$, $c = 0.6$, $d = 0-32$, $e = 0-1$, on the condition that a and b cannot be simultaneously equal to zero, and the process is conducted at a temperature of $320-440^\circ\text{C}$, pressure of 40-100 atm, initial gas space velocity in the reaction cycle of $200-1500 \text{ h}^{-1}$ with a volume ratio in the initial gas of $\text{CO}/\text{CO}_2 = 0-4$ and $\text{H}_2/\text{CO}_2 = 1-11$ and a mass ratio of the metal oxide component and zeolite of 50-70/30-50. 1 p. c., 4 tables.

The invention concerns organic chemistry, namely petrochemistry, and in particular, a method for production of hydrocarbon naphtha cuts by catalytic conversion of a mixture of CO_2 and H_2 and/or mixtures of CO_2 , CO , and H_2 . The naphtha cuts obtained can be used for practical purposes as automotive gasoline.

Most of the carbon emitted into the atmosphere is bound with oxygen as CO_2 . Most of the environmental carbon dioxide emissions occur in thermal power plants, metallurgical combines, and chemical and petrochemical plants. These plants frequently burn gaseous products consisting of more than 80 vol. % H_2 . Moreover, a large amount of natural gas is now processed for production of the hydrogen used in the nitrogen industry. Carbon dioxide is the basic by-product, and some of it is used for the different needs of the plant and is sold to consumers, while some of the commercial CO_2 is not marketed and is emitted into the atmosphere. A mixture of "extra" carbon dioxide and H_2 -containing flare gases could be used for production of additional chemical products and some of the stock resources of the plants could be saved in this way. Most CO_2 - and H_2 -containing industrial emissions also contain carbon monoxide, methane, or nitrogen as associated components, and their concentration in the gases can even exceed the concentration of carbon dioxide. In the conditions of industrial implementation of the invention to process CO_2 - and H_2 -containing gases into the hydrocarbon naphtha, no expensive treatment of the gases is necessary to remove the carbon monoxide in them.

A method for production of hydrocarbon naphthas from a gas mixture containing CO_2 , H_2 , and perhaps CO (as an associated component) which has a number of advantages in comparison to other methods is proposed in the present application.

There is already a method for production of different organic products, including hydrocarbon naphthas, from synthesis gas or a mixture of carbon dioxide and hydrogen [4].

According to the method in [4], a bifunctional catalyst containing zeolite in the dealuminized mordenite form and a composite of at least two transition elements such as copper, zinc, and chromium is used for conversion of synthesis gas or a mixture of CO_2 and H_2 .

The $\text{CO}_2 + \text{H}_2$ gas mixture ($\text{H}_2:\text{CO}_2 = 4:1$) is in contact with the catalyst at atmospheric pressure, temperature of 175-350°C, and space velocity of 3300 h^{-1} . The fundamental carbon-containing products of conversion of carbon dioxide are carbon monoxide, methanol, dimethyl ether, and methane. C_2+ hydrocarbons are totally absent in the products of the reaction. When the metal oxide composite and zeolite are placed in the reactor separately, the $\text{CO}_2 + \text{H}_2$ gas mixture is in contact with the metal oxides at temperatures of 200-250°C and the gas mixture subsequently obtained without separation passes through the bed of dealuminized mordenite at temperatures of 250-450° C. The pressure in the reactor is no higher than 1 atm and the space velocity of the $\text{CO}_2 + \text{H}_2$ mixture ($\text{H}_2:\text{CO}_2 = 4:1$) is maintained at the level of

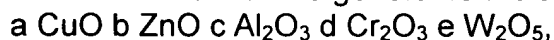
3330 h⁻¹. Organic products consisting of methanol, dimethyl ether, and a mixture of hydrocarbons are formed as a result of conversion of carbon dioxide. The content of the naphtha cut in all hydrocarbons formed is no greater than 30 wt. % and the molar amount of methanol formed is 5-10 times higher than the molar amount of hydrocarbon naphtha formed. A fundamental drawback of the method is the low selectivity of the process for hydrocarbon naphtha and the low degree of conversion of the gas mixture into organic products (less than 1%), which does not permit separating the hydrocarbon naphtha in commercial form in industrial conditions.

The method of conversion of synthesis gases into mixtures of hydrocarbons is closest to the invention in technical essence [1]. According to the selected prototype, mechanical Zn-Cr mixtures (or Zn-Cu-Cr(Al) or Zn-Cu-Cr-La) containing catalysts of synthesis of methanol and zeolite ZSM-5 (11, 12, 35, 38) are used for conversion of synthesis gas. Synthesis gas (H₂:CO = 0.2-6.0) is converted into a mixture of C₁-C₄ hydrocarbons (primarily C₁-C₄ paraffins) at pressures of 1-1000 atm, temperatures of 260-600°C, and initial synthesis gas space velocities with respect to the volume of catalyst loaded of 500-50,000 h⁻¹.

The following example from the prototype [1] is optimum for production of the naphtha cut. A mechanical mixture of a Cu-containing catalyst of synthesis of methanol and zeolite ZSM-5, with a volume ratio of Cu catalyst/ZSM-5 = 1/4, is used as the catalyst. The synthesis gas (H₂:CO = 2:1) is in contact with the catalyst at a pressure of 53 atm, temperature of 364°C, and initial synthesis gas space velocity with respect to the volume of catalyst loaded of 1210 h⁻¹. Conversion of CO and H₂ is 80% and 38%, respectively. Hydrocarbons of the following composition (wt. %) are obtained: methane, 4; ethane, 21; propane, 21; butanes, 17; pentanes, 10; other hydrocarbons (C₆₊), 27. The C₆₊ hydrocarbon fraction contains 34 wt. % aromatic hydrocarbons, which constitutes 25 wt. % on conversion to the C₅₊ fraction. Hydrocarbon naphtha with a relatively low concentration of aromatic hydrocarbons is obtained with this method, and the concentration of C₅₊ hydrocarbons in the total hydrocarbons formed does not exceed 37 wt. %. As a result, C₂-C₄ hydrocarbons are the basic hydrocarbon products of conversion of CO according to the prototype.

The object of the present invention is to produce hydrocarbon naphtha cuts with a high aromatic hydrocarbon content.

This goal is attained by using a catalyst with a metal oxide component containing three or more metal oxides with the general formula



where a, b, c, d, and e are the mass fractions of metal oxides in the metal oxide component, a = 0-56, b = 24-67, c = 0-6, d = 0-32, e = 0-1, in the condition that a and b cannot simultaneously be equal to zero, in the method for production of hydrocarbon naphtha cuts from gas containing H₂ and CO₂ or H₂, CO₂, and CO, by contact of the gas at a temperature of 320-440° C, pressure of 40-100 atm, and H₂/(CO+CO₂) volume ratio of 1-3, with a catalyst containing zeolite ZSM-5 or ZSM-11 and a metal oxide component, including zinc, copper, and/or chromium oxide, and conducting the

process at an initial gas space velocity of 200-1500 h⁻¹ with a volume ratio in the initial gas of CO/CO₂ = 0-4 and H₂/CO₂ = 1-1.

The problem is also solved by using a catalyst containing 30-50 wt. % zeolite and 50-70 wt. % metal oxide component.

The distinctive features of the invention are:

a) a catalyst containing a metal oxide component composed of three or more metal oxides of the general formula:



where a, b, c, d, and e are the mass fractions of metal oxides in the metal oxide component, a = 0-56, b = 24-67, c = 0-6, d = 0-32, e = 0-1, and a and b cannot simultaneously be equal to zero, is used in the method;

b) the process is conducted at the initial gas space velocity of 200-1500 h⁻¹;

c) the volume ratio in the initial gas is CO/CO₂ = 0-4 and H₂/CO₂ = 1-11;

d) a catalyst containing 30-50 wt. % zeolite and 50-70 wt. % metal oxide component is used.

The selection of the conditions of conducting synthesis of naphtha cuts from gas containing H₂ and CO₂ or H₂, CO₂, and CO is based on the following factors. The lower temperature limit, 320° C, is the limit of the minimum catalytic activity of the catalysts used in synthesis of aromatic hydrocarbons, and the upper temperature limit (440°C) is due to the onset of intense, irreversible deactivation of the metal oxide component of the catalyst. High pressure is required for the more exhaustive occurrence of intermediate reactions. The space velocity of the initial gas is determined by the activity of the catalyst used at fixed pressure and temperature. The claimed space velocity is optimum for production of the naphtha cut. The ratio between H₂ and CO₂ and between CO₂ and CO (when CO is present in the initial gas) is determined by the stoichiometry of the chemical reactions of synthesis of hydrocarbons. For example, for formation of a "CH₂" group in paraffinic hydrocarbons, two hydrogen atoms are necessary for each carbon atom, for synthesis of an aromatic ring, hydrogen consumption decreases by two times, and the presence of a bound "O" in the initial stock increases hydrogen consumption in formation of molecules of H₂O. Based on the theoretical premises, experiments were conducted in conditions sufficiently close to the stoichiometric ratio between "C", "O", and "H", and CO/CO₂ and H₂/CO₂ volume ratios in the initial gas of 0-4 and 1-11, respectively, were obtained experimentally based on the selectivity of the process for aromatic hydrocarbons.

Catalytic composites consisting of zeolite ZSM-5 or ZSM-11 and metal oxide composites in different combinations are used in the present invention; they allow

combining reactions of hydrogenation of carbon oxides and synthesis of hydrocarbons on one catalyst grain. The optimum mass ratio between zeolite and metal oxides in the catalyst was selected experimentally (see Table 1). The use of catalysts with different ratios between zeolite and metal oxide composite than those claimed in the invention will significantly worsen the indexes for the synthesis process, the naphtha cut, and the selectivity of the catalyst for aromatic hydrocarbons and hydrocarbon naphtha. The combination of three or more metal oxides in the metal oxide composite allows maximally converting the initial feedstock into intermediate methanol with high thermal and catalytic stability of work of the composite, chemical compounds containing Zn and Cu or Zn and Cr are the active component of the catalyst of synthesis of methane, and for this reason, the presence of Cu or Cr oxide together with Zn oxide in the catalyst is mandatory.

Experiments on conversion of synthesis gas and a mixture of CO₂ and H₂ were conducted on the same catalyst in the same conditions to compare the two processes for synthesis of naphtha cuts – from synthesis gas (similar to the prototype) and from a mixture of CO₂ and H₂. The catalyst and experimental conditions were selected based on the data in the prototype and the present invention. An example similar to the prototype is given below.

Example 1 (similar to the prototype). An isothermal reactor is filled with 120 cm³ of catalyst No. 1a with granulation of 3-4 mm. The initial gas mixture of the following composition (vol. %): H₂ 65.2, CO 34.3, and CH₄ is fed with a space velocity of 650 h⁻¹ (on conversion to the catalyst loaded) into the reactor unit for mixing with the gas circulating in the unit. The reactor unit consists of a reactor with a heater, reflux condenser, high- and low-pressure separators, intermediate liquid products container, and an electromagnetic pump for circulating the gas. The hydrocarbons are synthesized under a pressure of 80 atm and at a catalyst bed temperature of 400°C. To prevent uncondensed products from accumulating in the reactor unit, part of the reaction gas is constantly taken out of the unit after the high-pressure separator. The liquid products (naphtha cut, water, methanol), gas removed from the reactor unit, and gaseous hydrocarbons separated in throttling are analyzed separately by gas chromatography. The conditions and fundamental indexes of the experiment are reported in Table 2.

Catalyst No. 1a is prepared as follows. Powdered Zn–Cr catalyst (atomic ratio Zn:Cr = 2:1) is mixed with powdered high-silica zeolite ZSM-5 in the H form with the composition of 0.01 Na₂Al₂O₃ 34 SiO₂ in the mass ratio of 70/30. The mixture is granulated by extrusion with addition of 20 wt. % aluminum hydroxide. The catalyst extrudates are dried at 120°C for 4 h. The industrial applicability of the invention is illustrated by Examples 2-28.

Example 2. An isothermal reactor is loaded with 120 cm³ of catalyst No. 16 of 3-4 mm granulation. The initial gas mixture of the following composition (vol. %): H₂ 75.9, CO₂ 24.0, and N₂ 0.1, is fed into the reactor unit at a space velocity of 1000 h⁻¹ (on conversion to the loaded catalyst) for mixing with the gas circulating in the unit.

The reactor unit consists of a reactor with a heater, reflux condenser, high- and low-pressure separators, intermediate liquid product container, and an electromagnetic pump for circulating the gas. Synthesis of hydrocarbons is conducted at a pressure of 100 atm and catalyst bed temperature of 400°C. To prevent accumulation of uncondensed products in the reactor unit, part of the reaction gas is constantly evacuated from the unit after the high-pressure separator. The liquid products (naphtha cut, water, methanol), gas removed from the reactor unit, and gaseous hydrocarbons separated in throttling are analyzed separately by gas chromatography. The conditions and fundamental indexes of the experiment are reported in Table 3. Catalyst No. 16 is prepared as follows. Powdered Zn–Cr catalyst (atomic ratio Zn:Cr = 2:1) is mixed with powdered high-silica zeolite ZSM-5 in the H form with the composition of 0.01 Na₂O Al₂O₃ 34 SiO₂ in the mass ratio of 50/50. The mixture obtained is granulated by extrusion with addition of 20 wt. % aluminum hydroxide. The catalyst extrudates are dried at a temperature of 120°C for 4 h.

Examples 3-22. They are similar to Example 2. The conditions of the process are reported in Table 3 and the compositions of the catalysts are given in Table 1. Catalysts No. 4 and No. 1c are prepared similar to catalysts No. 1a and No. 16. Catalyst No. 2 is prepared as follows. Powdered Cu–Zn–Al catalyst is mixed with powdered high-silica zeolite ZSM-5 in the H form in the mass ratio of 70/30. The mixture is molded into pellets. The pellets are crushed to a 1-3 mm fraction. The preparation of catalyst No. 3 is similar to catalyst No. 2.

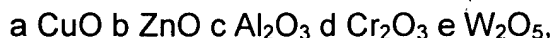
Examples 23-28. They are similar to Example 2. A mixture consisting of CO₂, CO, and H₂ in different ratios is used as the initial gas. The conditions of the process are reported in Table 4 and the compositions of the catalysts are given in Table 1. The value 1 (functional) is shown in Tables 2-4 to characterize the ratio of active components of the gas mixtures. The values of f are calculated with the equation:

$$f = \frac{H_2 - CO_2}{CO + CO_2} \text{ (volume/volume)}$$

As the examples and results in Tables 2-4 indicate, the use of CO₂ + H₂ or CO₂ + CO + H₂ instead of CO + H₂ (in the prototype) as the initial stock for production of hydrocarbon naphthas increases the content of aromatic hydrocarbons in the naphtha cut obtained and consequently increases its octane number in the conditions of the present invention.

CLAIMS

1. Method for producing naphtha hydrocarbons from gas containing H_2 and CO_2 or H_2 , CO_2 , and CO by contact of the gas at a temperature of 320-440°C, pressure of 40-100 atm, and $H_2/(CO + CO_2)$ volume ratio equal to 1-3 with a catalyst containing ZSM-5 or ZSM-11 zeolite and a metal oxide component including zinc, copper, and/or chromium oxide, characterized by the fact that a catalyst with a metal oxide component containing three or more metal oxides having the following general formula is used



where a, b, c, d, and e are the mass fractions of metal oxides in the metal oxide component, $a = 0-56$, $b = 24-67$, $c = 0-6$, $d = 0-32$, $e = 0-1$, on the condition that a and b cannot simultaneously be equal to zero, and the process is conducted at an initial gas space velocity of $200-1500 \text{ h}^{-1}$ with a volume ratio of $CO/CO_2 = 0-4$ and $H_2/CO_2 = 1-11$ in the initial gas.

2. Method according to claim 1, characterized by the fact that a catalyst containing 30-50 wt. % zeolite and 50-70 wt. % metal oxide component is used.

TABLE 1. Compositions of Catalysts Used

| Characteristics of catalyst components | | | | | | |
|---------------------------------------------------|------------------------------------------------------------------------------|----------------------------------------------------|-----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Catalyst No. | 1a | 2 | 3 | 4 | 1b | 1c |
| Composition (empirical formula) of zeolite | 0.01 Na ₂ O AL ₂ O ₃ 98SiO ₂ | | | 0.01 Na ₂ O AL ₂ O ₃ 0.3 Fe ₂ O ₃ 71SiO ₂ | 0.01 Na ₂ O AL ₂ O ₃ 34 SiO ₂ | 0.01 Na ₂ O AL ₂ O ₃ 200 SiO ₂ |
| Type of structure of zeolite | ZSM - 5 | | | ZSM - 10 | ZSM - 5 | |
| Composition of metal oxide composite (MC) (wt. %) | 67ZnO 32Cr ₂ O ₃ W ₂ O ₅ 5 | 56CuO 24ZnO 6 Al ₂ O ₃ | 38CuO 34ZnO 6 AL ₂ O ₃ 22 Cr ₂ O ₃ | 67ZnO 32Cr ₂ O ₃ 1W ₂ O ₅ 5 | | |
| MC/zeolite mass ratio | 70/30 | 50/50 | 70/30 | | 50/50 | |
| Binder and amount in catalyst (wt. %) | 20 AL ₂ O ₃ | | 20 AL ₂ O ₃ | | | |

TABLE 2. Experimental Conditions and Fundamental Indexes

| Example | 1 | 4 |
|----------------------------------------------|---------------------|----------------------------------|
| Initial stock | CO + H ₂ | CO ₂ + H ₂ |
| Catalyst No. | 1a | 1a |
| Initial gas space velocity, h ⁻¹ | 650 | 650 |
| Pressure, atm | 80 | 80 |
| Temperature, °C | 400 | 400 |
| Initial gas functional (f) | 1.9 | 1.9 |
| H ₂ /CO ₂ volume ratio | - | 2.9 |
| CO/CO ₂ volume ratio | - | 0 |
| Conversion, %: | | |
| CO | 83 | - |
| CO ₂ | - | 90 |
| H ₂ | 81 | 88 |
| Composition of hydrocarbons (HC), wt. %: | | |
| Methane | 2.5 | 4.5 |
| Ethane | 0.2 | 2.1 |
| Propane | 13.7 | 13.9 |
| Isobutane | 4.0 | 2.5 |
| <i>n</i> -Butane | 0.4 | 0.5 |
| CO ₅₊ in separation gases | 4.0 | 2.7 |
| Naphtha cut | 75.2 | 73.8 |
| Composition of naphtha cut, wt. %: | | |
| CO ₃ + CO ₄ | 1.9 | 2.6 |
| <i>n</i> -CO ₅₊ | 1.6 | 0.9 |
| Aromatic HC | 26.7 | 45.7 |
| Remaining CO ₅₊ | 69.9 | 50.8 |
| Motor method octane number of naphtha cut | 76 | 84 |

TABLE 3. Experimental Conditions and Fundamental Indexes

| Example | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------------------------------------------------------|------|------|------|------|------|------|------|
| Catalyst No. | 1b | 1a | 1a | 1a | 1a | 1a | 1a |
| Init. gas space velocity, h ⁻¹ | 1000 | 800 | 650 | 360 | 250 | 280 | 300 |
| Pressure, atm | 100 | 80 | 80 | 80 | 40 | 40 | 40 |
| Temperature, °C | 400 | 400 | 400 | 400 | 340 | 360 | 380 |
| Initial gas functional | 2.2 | 1.5 | 1.9 | 1.0 | 1.7 | 1.6 | 1.5 |
| H ₂ /(CO ₂ + CO) volume ratio | 3.2 | 2.5 | 2.9 | 2.0 | 2.7 | 2.6 | 2.5 |
| H ₂ /CO ₂ | 3.2 | 2.5 | 2.9 | 2.0 | 2.7 | 2.6 | 2.5 |
| CO/CO ₂ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Conversion, %: | | | | | | | |
| CO ₂ | 94 | 90 | 90 | 76 | 74 | 79 | 80 |
| H ₂ | 86 | 88 | 88 | 81 | 70 | 73 | 75 |
| Composition of products of reaction, wt. %: | | | | | | | |
| Hydrocarbons (HC) | 22.2 | 20.6 | 23.3 | 19.0 | 17.2 | 13.7 | 17.0 |
| H ₂ O | 70.8 | 72.3 | 66.7 | 62.3 | 64.3 | 65.3 | 61.0 |
| CO | 4.4 | 6.2 | 7.4 | 17.4 | 16.9 | 18.1 | 19.1 |
| CH ₃ OH + (CH ₃) ₂ O | 2.6 | 0.9 | 2.6 | 1.3 | 1.6 | 2.9 | 2.1 |
| Composition of hydrocarbons, wt. % | | | | | | | |
| Methane | 2.8 | 6.9 | 4.5 | 6.5 | 2.2 | 6.7 | 6.5 |
| Ethane | 0.3 | 3.6 | 2.1 | 3.1 | 1.6 | 2.0 | 2.5 |
| Propane | 16.0 | 4.2 | 13.9 | 39.9 | 28.6 | 14.0 | 17.5 |
| Isobutane | 5.6 | 3.6 | 2.5 | 4.9 | 6.8 | 5.3 | 5.6 |
| <i>n</i> -Butane | 1.4 | 1.2 | 0.5 | 1.2 | 0.5 | 0.7 | 0.8 |
| CO ₅₊ HC in separation gases | 2.5 | 4.8 | 2.7 | 5.9 | 7.2 | 8.0 | 6.6 |
| Naphtha cut | 71.4 | 75.7 | 73.8 | 38.5 | 53.2 | 63.3 | 60.5 |
| Composition of naphtha cut, wt. % | | | | | | | |
| CO ₃ + CO ₄ | 2.3 | 3.6 | 2.6 | 0.6 | 0.2 | 0.2 | 0.3 |
| <i>n</i> -CO ₅₊ | 0.1 | 0.9 | 0.9 | 0.5 | 0.1 | 0.1 | 0.3 |
| Aromatic HC | 46.9 | 43.7 | 45.7 | 73.0 | 71.3 | 65.8 | 60.2 |
| Remaining CO ₅₊ | 50.7 | 51.8 | 50.8 | 25.9 | 28.4 | 34.0 | 39.2 |

Table 3 (cont.)

| Example | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|--------------------------------------------------------|------|------|------|------|------|------|------|
| Catalyst No. | 1a | 1a | 1a | 1a | 1a | 1a | 1a |
| Init. gas space velocity, h ⁻¹ | 400 | 700 | 500 | 400 | 300 | 550 | 630 |
| Pressure, atm | 40 | 60 | 60 | 60 | 60 | 80 | 80 |
| Temperature, °C | 400 | 400 | 380 | 360 | 340 | 380 | 360 |
| Initial gas functional | 1.8 | 2.2 | 2.3 | 2.2 | 1.9 | 1.9 | 2.1 |
| H ₂ /(CO ₂ + CO) volume ratio | 2.8 | 3.2 | 3.3 | 3.2 | 2.9 | 2.9 | 3.1 |
| H ₂ /CO ₂ | 2.8 | 3.2 | 3.3 | 3.2 | 2.9 | 2.9 | 3.1 |
| CO/CO ₂ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Conversion, %: | | | | | | | |
| CO ₂ | 87 | 90 | 89 | 88 | 80 | 88 | 91 |
| H ₂ | 81 | 89 | 84 | 80 | 74 | 86 | 88 |
| Composition of products of reaction, wt. %: | | | | | | | |
| Hydrocarbons (HC) | 19.5 | 22.0 | 21.5 | 18.4 | 13.4 | 22.1 | 20.4 |
| H ₂ O | 64.1 | 68.9 | 66.0 | 66.3 | 67.8 | 66.8 | 69.3 |
| CO | 14.2 | 6.8 | 9.6 | 12.0 | 15.7 | 9.0 | 7.7 |
| CH ₃ OH + (CH ₃) ₂ O | 2.2 | 2.3 | 2.9 | 3.3 | 3.1 | 2.1 | 2.6 |

Table 3 (cont.)

| Example | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|-----------------------------------------|------|------|------|------|------|------|------|
| Composition of hydrocarbons, wt. % | | | | | | | |
| Methane | 6.9 | 4.9 | 3.7 | 5.1 | 1.6 | 5.9 | 3.2 |
| Ethane | 3.0 | 2.9 | 1.8 | 2.0 | 2.2 | 3.2 | 2.1 |
| Propane | 10.0 | 9.4 | 11.5 | 10.5 | 10.3 | 17.1 | 12.7 |
| Isobutane | 6.3 | 2.9 | 3.3 | 3.2 | 1.2 | 2.9 | 2.1 |
| <i>n</i> -Butane | 1.2 | 0.5 | 0.5 | 0.5 | 0.2 | 0.6 | 0.5 |
| CO ₅₊ HC in separation gases | 8.4 | 2.8 | 4.0 | 4.0 | 2.3 | 2.7 | 2.8 |
| Naphtha cut | 64.2 | 76.6 | 75.2 | 74.7 | 82.2 | 67.6 | 76.6 |
| Composition of naphtha cut, wt. % | | | | | | | |
| CO ₃ + CO ₄ | 2.0 | 3.5 | 2.5 | 0.8 | 0.2 | 0.9 | 0.7 |
| <i>n</i> -CO ₅₊ | 0.2 | 1.2 | 0.4 | 0.4 | 0.2 | 0.8 | 1.7 |
| Aromatic HC | 44.1 | 46.0 | 39.9 | 57.0 | 70.0 | 56.4 | 57.2 |
| Remaining CO ₅₊ | 53.7 | 49.3 | 57.2 | 41.8 | 29.6 | 41.9 | 40.4 |

Table 3 (cont.)

| Example | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|--------------------------------------------------------|------|------|------|------|------|------|------|
| Catalyst No. | 1a | 1a | 1c | 4 | 3 | 2 | 2 |
| Init. gas space velocity, h ⁻¹ | 330 | 250 | 360 | 700 | 530 | 480 | 470 |
| Pressure, atm | 80 | 80 | 80 | 80 | 80 | 80 | 80 |
| Temperature, °C | 340 | 320 | 440 | 420 | 400 | 380 | 360 |
| Initial gas functional | 2.2 | 2.2 | 1.0 | 1.9 | 1.9 | 2.1 | 2.0 |
| H ₂ /(CO ₂ + CO) volume ratio | 3.2 | 3.2 | 2.0 | 2.9 | 2.9 | 3.1 | 3.0 |
| H ₂ /CO ₂ | 3.2 | 3.2 | 2.0 | 2.9 | 2.9 | 3.1 | 3.0 |
| CO/CO ₂ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Conversion, %: | | | | | | | |
| CO ₂ | 84 | 76 | 80 | 93 | 89 | 92 | 88 |
| H ₂ | 76 | 67 | 83 | 90 | 92 | 88 | 89 |
| Composition of products of reaction, wt. %: | | | | | | | |
| Hydrocarbons (HC) | 17.8 | 16.3 | 20.5 | 20.8 | 26.9 | 27.1 | 22.7 |
| H ₂ O | 64.8 | 65.0 | 63.0 | 72.3 | 67.9 | 65.5 | 65.7 |
| CO | 14.2 | 15.2 | 15.5 | 5.2 | 2.9 | 3.8 | 4.3 |
| CH ₃ OH + (CH ₃) ₂ O | 3.2 | 3.5 | 1.0 | 1.7 | 2.3 | 3.6 | 7.3 |
| Composition of hydrocarbons, wt. % | | | | | | | |
| Methane | 4.2 | 1.4 | 7.4 | 3.7 | 13.2 | 8.9 | 7.0 |
| Ethane | 3.3 | 3.1 | 3.0 | 1.9 | 5.7 | 6.3 | 4.3 |
| Propane | 13.7 | 21.9 | 31.0 | 9.0 | 12.6 | 11.4 | 17.4 |
| Isobutane | 2.7 | 1.6 | 5.1 | 4.0 | 6.9 | 7.6 | 10.4 |
| <i>n</i> -Butane | 0.7 | 0.3 | 1.0 | 0.7 | 1.7 | 1.9 | 2.6 |
| CO ₅₊ HC in separation gases | 4.3 | 3.9 | 6.0 | 2.0 | 8.0 | 7.6 | 4.3 |
| Naphtha cut | 71.1 | 67.8 | 46.5 | 78.7 | 51.9 | 56.3 | 54.0 |
| Composition of naphtha cut, wt. % | | | | | | | |
| CO ₃ + CO ₄ | 0.3 | 0.1 | 1.3 | 2.5 | 0.8 | 0.6 | 0.5 |
| <i>n</i> -CO ₅₊ | 0.2 | 0.1 | 0.2 | 1.0 | 1.6 | 1.7 | 1.3 |
| Aromatic HC | 69.6 | 83.7 | 68.7 | 42.3 | 42.3 | 43.8 | 61.2 |
| Remaining CO ₅₊ | 29.9 | 16.1 | 29.8 | 54.2 | 55.3 | 53.9 | 37.0 |

TABLE 4. Experimental Conditions and Fundamental Indexes

| Example | 23 | 24 | 25 | 26 | 27 | 28 |
|--------------------------------------------------------|------|------|------|------|------|------|
| Catalyst No. | 1a | 1a | 1a | 1a | 1a | 1a |
| Init. gas space velocity, h ⁻¹ | 1150 | 550 | 400 | 320 | 250 | 450 |
| Pressure, atm | 80 | 80 | 80 | 80 | 80 | 40 |
| Temperature, °C | 400 | 400 | 400 | 400 | 400 | 400 |
| Initial gas functional | 2.1 | 1.5 | 1.3 | 1.0 | 0.7 | 2.1 |
| H ₂ /(CO ₂ + CO) | 2.4 | 1.8 | 1.7 | 1.5 | 1.2 | 2.3 |
| H ₂ /CO ₂ | 6.8 | 4.9 | 4.2 | 3.0 | 2.2 | 10.9 |
| CO/CO ₂ | 1.8 | 1.6 | 1.4 | 1.0 | 0.7 | 3.8 |
| Conversion, % | | | | | | |
| CO ₂ | 91 | 80 | 61 | 59 | 52 | 62 |
| CO | 90 | 78 | 64 | 49 | 28 | 74 |
| H ₂ | 93 | 86 | 81 | 78 | 74 | 82 |
| Composition of products of reaction, wt. % | | | | | | |
| Hydrocarbons (HC) | | | | | | |
| H ₂ O | 30.1 | 29.0 | 31.1 | 37.8 | 41.4 | 35.2 |
| CH ₃ OH + (CH ₃) ₂ O | 67.3 | 61.4 | 66.4 | 58.7 | 56.9 | 58.8 |
| | 2.6 | 9.6 | 2.5 | 3.5 | 1.7 | 6.0 |
| Composition of hydrocarbons, wt. %: | | | | | | |
| Methane | 4.0 | 5.7 | 12.1 | 14.5 | 14.3 | 14.0 |
| Ethane | 1.1 | 1.3 | 2.9 | 2.9 | 4.5 | 2.8 |
| Propane | 4.5 | 7.1 | 5.8 | 23.3 | 18.7 | 12.6 |
| Isobutane | 0.9 | 1.0 | 2.3 | 2.7 | 4.5 | 3.5 |
| <i>n</i> -Butane | 0.2 | 0.2 | 0.9 | 0.8 | 1.6 | 0.8 |
| CO ₅₊ in separation gases | 1.2 | 1.5 | 3.2 | 4.7 | 9.5 | 3.3 |
| Naphtha cut | 88.1 | 83.2 | 72.8 | 51.1 | 46.9 | 63.0 |
| Composition of naphtha cut, wt. % | | | | | | |
| CO ₃ + CO ₄ | 2.2 | 1.0 | 0.8 | 0.6 | 0.5 | 1.0 |
| <i>n</i> -CO ₅₊ | 0.2 | 0.8 | 0.6 | 0.5 | 0.4 | 0.7 |
| Aromatic HC | 45.7 | 58.9 | 72.9 | 71.9 | 83.1 | 55.2 |
| Remaining CO ₅₊ | 51.9 | 39.3 | 25.7 | 27.0 | 16.0 | 43.1 |